

AD-A116 933

WISCONSIN UNIV-MILWAUKEE DEPT OF CHEMISTRY  
FIFTH INTERNATIONAL SUMMER INSTITUTE IN SURFACE SCIENCE (ISSS -ETC(U)  
JUL 82 R VANSLOW

F/8 7/8

N00014-81-8-8889

ML

UNCLASSIFIED

[01]

0 0 0



END

DATE

FILED

82

DTIC

AD A116933

DTIC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER N0014-81-G-0059	2. GOVT ACCESSION NO. <b>AD-A116933</b>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Fifth International Summer Institute in Surface Science (ISISS 1981)	5. TYPE OF REPORT & PERIOD COVERED Final	
7. AUTHOR(s) Professor Ralf Vanselow	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Wisconsin-Milwaukee Milwaukee, Wisconsin 53201	8. CONTRACT OR GRANT NUMBER(s) N0014-81-G-0059	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 392-030	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) ONR Branch Office-Chicago 536 S. Clark Street Chicago, IL 60605	12. REPORT DATE 8 July 1982	
	13. NUMBER OF PAGES 20	
	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A	
16. DISTRIBUTION STATEMENT (of this Report)  Distribution of this document is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  Distribution of the abstract is unlimited		
18. SUPPLEMENTARY NOTES To be published by Springer Verlag, Berlin-Heidelberg-New York under the title: "Chemistry and Physics of Solid Surfaces, Volume IV".		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) ISISS 1981, Chemisorption, Physisorption, Surface Analytical Techniques, Surface Defects, Theoretical Aspects of Surfaces, Thermal and Field Desorption, Surface and Internal Segregation.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) At the Fifth International Summer Institute in Surface Science, twenty leading scientists presented tutorial review talks on gas-solid and solid-solid interfaces. Paper topics: "Development of Photoemission as a Tool for Surface Analysis - From Semiconductors to Catalysis"; "Auger Spectroscopy as a Probe of Valence Bands"; "Laser Fluorescence Spectroscopy of Sputtered Atoms"; "Chemisorption Investigated by Ellipsometry"; "He Atom Diffraction from Semiconductor Surfaces"; "Electron Energy Loss Spectroscopy of Surface Vibrations"; "High resolution		

DD FORM 1 JAN 73 1473

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

82 JUL 15 1982

12

DTIC  
ELECT  
JUL 15 1982

20. (cont.)

LEED Studies of Adsorbed Films; UHV Electrochemistry; "Field Desorption and Photon-Induced Field Desorption"; "Thermodesorption"; "Monte Carlo Simulations of Chemisorbed Overlayers"; "Critical Phenomena of Chemisorbed Overlayers"; "Some Theoretical Aspects of Metal Clusters, Surfaces and Chemisorption"; "Electronic Aspects of Adsorption Rates"; "Impact of Steps and Imperfections on Surface Studies"; "The Use of Electron Microscopy in Surface Science"; "SIMS of Reactive Surfaces"; "Electronegativity -- A Useful Concept in Surface Chemistry"; "Surface Segregation Studied by Low Energy Ion Scattering"; "Effects of Internal Surface Adsorption on Metallurgical Properties"

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	



Report N0014-81-G-0059

FIFTH INTERNATIONAL SUMMER INSTITUTE IN SURFACE SCIENCE

(ISISS 1981)

Professor Ralf Vanselow, Director  
Department of Chemistry  
University of Wisconsin--Milwaukee  
Milwaukee, Wisconsin 53201

Final Report for the period 15 April 1981 - 14 April 1982

The academic goals of ISISS were outlined in the editorial comments of "Surface Science: Recent Progress and Perspectives (ISISS 1975)":

"The favorable acceptance of ISISS was gratifying, but did not exactly come as a surprise. During the recent decade, advanced ultrahigh vacuum technology has made the achievement of pressures  $\leq 10^{-10}$  Torr a routine operation so that surfaces, once freed from impurities, can be kept clean over a sufficient length of time and adsorbates then can be admitted at well-dosed amounts. Techniques for surface analysis were more and more refined; with the atom probe we are now able to analyze even single surface atoms or chemical complexes. Progress in the theory of the solid state subsequently allowed some fruitful dealing with the theoretical aspects of solid surfaces. All these developments combined with the demand for data by vital branches of our modern technology, caused an increasing flood of publications especially in the field of gas-solid interfaces. It became hard to catch up with the literature in one's own narrow area and it appeared nearly impossible to keep track of the developments in neighboring fields. As in other fast developing parts of the natural sciences, one consequently observes some isolationism and the appearance of communication problems. It is quite clear that such a tendency, where one no longer learns from progress or setbacks in neighboring areas, would be very much to our disadvantage. To counteract this tendency, ISISS was organized. Leading experts from various subdivisions of surface science - we chose to restrict the topics to gas-solid interfaces - presented tutorial review talks in which recent progress was summarized and future trends were pointed out."

In order to keep ISISS 1981 at a level of highest quality all former ISISS speakers were invited to suggest names of suitable lecturers. To avoid duplication, none of the lecturers of the 1979 Summer Institute were invited to present a paper. The final list showed twenty-one internationally known experts in the field of gas-solid (solid-solid) interfaces. The speakers came from Belgium, Germany, The Netherlands, Northern Ireland, the United Kingdom, and from the U.S.A.

The following list shows their names, their affiliations, topics, and short summaries of the papers presented. (Because of illness Dr. J. J. Rooney was unable to present his lecture).

Gosse A. Bootsma, Twente University of Technology, Enschede, The Netherlands

### Chemisorption Investigated by Ellipsometry

A comparison of the various probes applied in surface investigations indicates that photons, in and around the visible region of the spectrum, are generally less atom-specific and less surface-sensitive than electrons and ions. Moreover, the limit of detection of optical techniques is usually larger than in electron or ion spectroscopy. However, in contrast with electrons or ions the influence of photons on the studied samples and processes is generally negligible and in situ measurements at high gas pressures or with liquids are possible.

Ellipsometry involves the measurement of the change in the state of polarization that occurs when a polarized, monochromatic light beam is reflected at an interface. Basically one measures the two parameters  $\Delta$  and  $\psi$  defined by  $\tan\psi \exp(i\Delta) = r_p/r_s$ , where  $r_p$  and  $r_s$  are the amplitude reflection coefficients for light polarized parallel and perpendicular to the plane of incidence. For a clean substrate the measurement yields the complex refractive index or dielectric constant, for a substrate covered with a layer information is obtained on the optical parameters and thickness of this layer. The observed changes in  $\Delta$  and  $\psi$  upon adsorption enable one to monitor (sub)monolayer surface coverages. Calibration against other techniques (e.g., AES, LEED) makes it possible to determine, e.g., the kinetics of chemisorption and of surface reactions and the initial stages of oxidation. For the physical interpretation of the results (nature of the adsorbed layer, substrate changes induced by chemisorption) measurements at various wavelengths have to be performed.

A review will be given of ellipsometric studies in ultra high vacuum systems of chemisorption processes on metal and semiconductor surfaces.

J. H. Block, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

### Field Desorption and Photon-Induced Field Desorption

Field desorption processes are studied by applying different mass spectrometric devices. Besides mass determination of desorption products the integral energy distribution is measured. The high energy onset in energy distribution (appearance spectroscopy) provides information on energies of ion generating processes. Experimental results will be discussed for reactions of hydrogen and carbon monoxide with metal surfaces.

Field desorption is enhanced by electron or photon impact. The influence of impinging electrons is studied by using an auxiliary gas with relatively low ionization potential, which is ionized in space in

front of the emitter and which is providing electrons for impact. Another way of exciting molecules in an adsorbed layer is followed by using photon-pulses of a laser source. In this case, the photon induced field desorption is measured by a time correlated time-of-flight determination.

Several reactions will be discussed like polymerization of ethene, formation of metal cluster-ions and of complex-ions.

C. L. Briant, General Electric Company, Corporate Research and Development Center, Schenectady, New York

#### The Effects of Internal Surface Adsorption on Metallurgical Properties

- I. General reasons for metallurgical interest in this problem
- II. Basic studies of segregation to grain boundaries and particle matrix interfaces.
  - A. Experimental results - Emphasis will be on iron base systems. Results on nickel and copper alloys will also be presented.
  - B. Effects of grain boundary structure on segregation.
  - C. Theories used to explain grain boundary segregation.
    1. Causes of segregation
    2. Kinetics of segregation
- III. Metallurgical Applications
  - A. Fracture - Temper embrittlement will be used as an example of intergranular fracture and ductile fracture will be used as an example of fracture along the particle-matrix interface.
  - B. Corrosion - Phosphorus induced corrosion will be used as an example of intergranular corrosion and pitting will be used as an example of corrosion at a particle-matrix interface.
  - C. Grain growth - Grain growth controlled by segregated nitrogen in Fe-3%Si will be used as an example.

T. M. Buck, Bell Laboratories, Murray Hill, New Jersey

#### Surface Segregation Studied by Low Energy Ion Scattering

- I. Surface Segregation in Binary Alloys  
 Equilibrium surface enrichment by one component of an alloy, only recently recognized as a very general phenomenon, has been explained by bond-breaking as formalized, for example, in the Regular Solution model, also by lattice strain induced by

differences in atom size, and by various combinations of these driving forces. These models and some predictions based on them will be reviewed briefly.

II. Surface Techniques Used

Since the segregation is confined to the first few atom layers, sometimes the first only, unusual surface sensitivity is required for analysis, such as that first only, unusual surface sensitivity is required for analysis, such as that possessed by low energy ion scattering, the atom-probe-field-ion microscope, and Auger electron spectroscopy. Some advantages and disadvantages of these techniques will be mentioned.

III. Principals of Low Energy Ion Scattering

The time-of-flight version LEIS (TOF), which collects both scattered neutrals and ions will be emphasized. It facilitates quantitative interpretation by circumventing the neutralization questions which accompany electrostatic analysis of noble gas ions. It also reduces the ion flux required, and on single crystal surfaces, permits sampling of one, two, or three atom layers depending on direction of incidence of the ion beam.

IV. Results on Polycrystalline Samples of CuNi, CuPt, and AuNi.  
Comparisons with predictions of various models.

V. Results on Single Crystal Alloys. Ni{001}Au, Fe{001}Sn, Cu<sub>3</sub>Au{001} and {001}. Layer compositions, atomic arrangement of segregated layer, competition between ordering and segregation in case of Cu<sub>3</sub>Au{001} and {011}.

M. J. Cardillo, Bell Laboratories, Murray Hill, New Jersey

He Diffraction from Semiconductor Surfaces

The scattering of thermal energy He beams from semiconductor surfaces will be reviewed. The focus will be an assessment of the development of He diffraction into a quantitative structural probe. Results for the Si{100} surface showing a disordered (2x1) periodicity will be discussed. The calibration experiment on the known GaAs{110} surface will be described and include new developments on the theory of atom diffraction and the calculation of the He-surface potential. A model of the Si{111} 7x7 surface based on He scattering will also be presented and discussed.

W. N. Delgass, Purdue University, West Lafayette, Indiana

SIMS of Reactive Surfaces

- I. Introduction
  - A. Review of basic processes
  - B. Review of Winograd, Garrison, Harrison Calculations
  - C. Review of SIMS of molecular solids
  - D. Summary of SIMS characteristics
- II. Applications to flat surfaces
  - A. Sensitivity to surface chemistry
  - B. Sensitivity to structure
  - C. Sensitivity reaction intermediates
  - D. CO, H<sub>2</sub> chemistry on Ru (001)
- III. Applications to Catalysis
  - A. Complex oxides
  - B. Supported metals
  - C. Molecular structure on complex surfaces
  - D. Proximity analysis
- IV. Conclusions and Outlook for the Future
  - A. Flat surfaces
  - B. Catalysts

Theodore L. Einstein, University of Maryland, College Park, Maryland

Critical Phenomena of Chemisorbed Overlayers

- I. Chemisorbed Overlayers as Lattice Gas System with Fixed Coverage
  - A. Distinctions from physisorption (to the extent not covered by Roelofs)
    - 1. Relationship of key energies
    - 2. Implications for what is controlled in experiments
    - 3. Implications for incommensuration
    - 4. Implications for variety of structures and available measurables
    - 5. LEED as ideal probe of ordering of atoms on single crystal surfaces
  - B. Parametrization of Microscopic Hamiltonian
    - 1. Brief Synopsis of developments as of ISISS 1977
    - 2. Recent progress
      - a) Jellium
      - b) Embedded clusters (Muscat-Newns)
      - c) Special cases (Haydock & Gallagher, Theodorou)
      - d) Elastic
    - 3. Comments on long-range character

- II. Features of phase diagrams (to the extent not covered by Roelofs)
  - A. Repulsive interactions only
    - 1. Narrow ordered regimes
    - 2. Second-order transitions when possible - [lines of] critical points
    - 3. Relation to percolation thresholds
  - B. Attractive interactions also - ordered phase at low coverage
    - 1. First-order phase transitions
    - 2. Nature of mixed phase region
      - a) Spinodal decomposition
      - b) Island size limitations
      - c) Experimental results
    - 3. Tricritical points
  - C. Effects of 3-atom interactions
    - 1. Gross phase asymmetries
    - 2. High-temperature asymmetries not necessarily automatic or pronounced.
- III. Critical Exponents
  - A. Order parameter
  - B. Review of exponents, analogies with magnets, fluids
  - C. Universality classes
    - 1. Landau-Ginzburg-Wilson free energy expansion
    - 2. Classifications for adlayers by Domany, Schick, Walker, et al.
    - 3. Intuitive picture from interacting Kadanoff blocks (Alexander)
  - D. Determination of exponents via LEED
    - 1. Beam profile measurements
    - 2. Removal of instrument response function
    - 3. Comparison with X-rays, neutrons
    - 4. Requirements for physical system
  - E. Case study:  $p(2 \times 2)$ -O/Ni{111} - Only chemisorbed system examined to date for exponents
    - 1. Predictions
    - 2. Experimental results
    - 3. Possible adjustments: corrections to scaling, Fisher renormalization
    - 4. Surface defects: steps, point defects
    - 5. Subtle reconstructions
  - F. Goals
    - 1. Accessible 2-D transition for comparison with lattice gas models
    - 2. Extent of well-ordered substrate region
    - 3. Nature of disordering - interplay of micro and macro
    - 4. High-resolution LEED

S. C. Fain, Jr., University of Washington, Seattle, Washington

High Resolution LEED Studies of Adsorbed Films

- 1) Introduction to physical adsorption on graphite
- 2) Development of U.W. apparatus (conceived at ISIS 1973)
- 3) Krypton on graphite: Commensurate-incommensurate Transition
- 4) Argon on graphite: Rotational epitaxy of an Incommensurate monolayer
- 5) Argon on graphite: Thermodynamic properties of an incommensurate monolayer vis-a-vis U. Wisconsin work by Bruch and Webb for films on Ag{111}.
- 6) Neon on graphite: Work of Caliste and Suzanne from Marseille
- 7) Commensurate-incommensurate transition of Xe on Cu{110}: Jaubert, Glachant, Bienfait, and Boato from Marseille
- 8) Orientational Ordering of N<sub>2</sub> Molecular Axes in the Commensurate Phase
- 9) Possible future directions for Physical Adsorption Studies by LEED

Dieter M. Gruen, Chemistry Division, Argonne National Laboratory, Argonne, Illinois

Laser Fluorescence Spectroscopy of Sputtered Atoms and Other Applications of Lasers to Surface Science

The impact of lasers on surface science has been in two chief areas. The first is that of laser induced surface reactions and the second that which may broadly be called laser spectroscopy of surfaces.

This paper will deal primarily with laser fluorescence spectroscopy (LFS) of sputtered atoms. However, some mention will also be made of the other applications of lasers to the study of surfaces.

In the field of laser induced surface reactions, the ability to deposit energy in precisely controllable time and space domains is the

key to success. Thus materials processing (heat-treatment of alloys and forgings, cutting, welding, drilling, etc.) has already matured into commercial practice. Laser annealing of defects in ion-implanted silicon and surface etching of LSI circuit materials by laser generated neutral species has been demonstrated. The production of sinterable ceramic powders by CO<sub>2</sub>-laser-driven gas phase reactions and "laser-plasma spraying" processes for applying refractory coatings to materials are in the offing as are photochemically deposited thin metallic films with better than 1  $\mu$ m definition. A potentially exciting field is laser control of reactions at or near catalytic surfaces. Some results have been reported but the detailed mechanisms are still unclear.

An important discovery in the field of surface science has been the observation of enormously enhanced cross sections (up to factors of 10<sup>6</sup>) for Raman scattering from molecules adsorbed on metal surfaces. This so-called Surface Enhanced Raman Spectroscopy (SERS) enables the determination of detailed structural information about adsorbed molecules even in sub-monolayer coverages, and in both solid-gas and solid-liquid environments. Although SERS has been a subject of intense study, its interpretation is still controversial with at least six alternative mechanisms under active consideration.

Recent experiments have demonstrated that Doppler-shift laser induced fluorescence spectroscopy can provide a sensitive, high resolution and facile method for obtaining both sputtered neutral atom number density velocity distributions and relative sputtering yields. These findings have led in turn to the development of LFS as a promising technique for the study of impurity atoms emanating from surfaces exposed to fusion plasmas. Little is known about the generation and fate of high Z impurities despite their marked deleterious effects on plasma power balance. Tuneable lasers, either pulsed or c.w. make it possible, in principle, to determine most of the elements in the periodic table by exciting resonance transitions and observing spontaneous fluorescence emission. Impurity density and velocity distribution information is potentially available from such data during a single plasma discharge by Doppler scanning the laser light frequency. Results from laboratory experiments as well as from in situ measurements on Tokamaks will be presented. For example, the LFS technique has been used to determine the Zr-atom density generated from a Zr-metal target during a single Tokamak discharge (APEX: 100 ms pulse duration, 40 kA plasma current) with 1 ms sampling interval and 1 mm spatial resolution. The Zr-atom velocity distribution was measured via the Doppler shift technique. Most of the data were obtained by pumping a  $J \rightarrow J'$  component of the  $a^3F \rightarrow 3F_0$  manifold with observation of fluorescence at  $|\Delta J| = 1$ . Thus, both scattered light and line broadening due to Zeeman splitting was minimized. A c.w. ring dye laser provided the high duty cycle, narrow velocity resolution (10m/sec) and saturating power required for these measurements. In order to discriminate against fluctuations in background plasma emission, 100 kHz acousto-optic modulation of the laser intensity was employed with a 4-channel microcomputer-controlled 100 MHz scalar system.

It can be seen that lasers are already useful in various aspects of surface science and can be expected to find wider fields of applications to surface related phenomena in the future.

O. Gunnarsson, Max-Planck-Institut für Festkörperforschung, Stuttgart,  
Federal Republic of Germany

#### Electronic Aspects of Adsorption Rates

After a brief introduction, I will discuss some recent ideas, in particular by Nørskov and Lundqvist, about when electronic processes may be important for energy accommodation. I will then focus on theoretical methods for treating the excitation of electron-hole pairs, and show that for a slow external perturbation the excitations can be treated as bosons. This leads to simple results for the energy accommodation, and the general features of these results will be discussed. I will also talk about the validity of these boson approximations and show how temperature effects are included. Finally, using numerical calculations, I will discuss the importance of electronic effects in a few cases.

M. G. Lagally, University of Wisconsin--Madison, Madison, Wisconsin

#### Impact of Steps and Imperfections on Surface Studies

A number of structural defects are possible on clean surfaces, in adsorbed submonolayers, and in thicker, epitaxially grown films. These include some that are unique to surfaces, such as steps, others that are the two-dimensional analogue of three-dimensional defects, such as finite island sizes or antiphase boundaries in overlayers, and still others that are the manifestation at the surface of bulk defects, such as slip planes, subgrain size effects, and strain. Such defects can affect a variety of surface or overlayer electronic and chemical properties and can alter surface kinetic and thermodynamic processes. The identification and the quantification of surface structural defects, mostly by LEED, are described. Recent measurements of surface defects in metals and semiconductors are described. Examples of the influence of surface defects or other surface properties are discussed with emphasis on phase transitions in overlayers, nucleation and epitaxy, and electronic properties.

Dietrich Menzel, Technische Universität München, Germany

#### Thermal Desorption

The investigation of the kinetics of thermal desorption will be reviewed with respect to experimental methods and interpretation of the

results; some theoretical concepts will also be sketched. The connection between kinetic parameters and statistical properties of the adlayer will be emphasized. Some recent developments (improvements of experimental techniques; importance of precursors and of nonequilibrium states; energy transfer via vibrational and electronic coupling) will be discussed.

R. P. Messmer, General Electric Corporate Research and Development,  
Schenectady, New York

#### Some Theoretical Aspects of Metal Clusters, Surfaces

- I. Comparison of theoretical results for metal clusters using different molecular orbital methods
  - A. Theoretical Methods
    - Density Functional/ $X_\alpha$
    - Hartree Fock
    - Semi-empirical molecular orbital methods
  - B. Intrinsic properties of metal clusters
    - Densities of states
    - Magnetic behavior
- II. Clusters as models of metal surfaces
  - A. Chemisorption of O on Al
  - B. Chemisorption of CO on Cu

D. L. Mills, University of California--Irvine, Irvine, California

#### Electron Energy Loss Spectroscopy of Surfaces

The talk will outline the applications of high resolution electron energy loss spectroscopy in surface physics, with emphasis on the principal concepts required in the interpretation of the spectra. For small deflection angles and energy losses, the dominant source of coupling between the electron and the surface excitations has its origin in the oscillating electric dipole moment of the latter. Some examples of spectra and their interpretation will be examined. When the angular deflection of the electron is large, then a fully microscopic analysis is required for the description of the electron solid interaction. We shall discuss recent theoretical work in this area on the inelastic scattering of electrons by adsorbate vibrations, for systems of current experimental interest. Throughout the discussion, we shall place emphasis on selection rules which operate, and with data that illustrates them.

David E. Ramaker, George Washington University, Washington, D.C.

Auger Spectroscopy as a Probe of Valence Electrons

- I. Introduction
  - A. Auger lineshape interpretation - Is it worth it?
    - 1. Complements AES and XES
    - 2. Experimentally convenient
  - B. Scope of review
- II. One electron semi-empirical LCAO-MO theory
  - A. Auger electron energy
    - 1. Empirical MO energies
    - 2. Hole-hole repulsion and relaxation
    - 3. Multiplet splitting
  - B. Auger intensity
    - 1. Atomic Auger matrix elements
      - a. Examination of relative intensities with Z
      - b. Comparison with theory
    - 2. Populations - local or Mulliken
  - C. Auger line widths
    - 1. Valence band widths
    - 2. Core hole lifetime broadening
    - 3. Nuclear broadening
    - 4. Instrumental broadening
- III. Correlation effects
  - A. Hole localization
    - 1. U vs  $\Gamma$
    - 2. Metals
    - 3. Covalent/ionic molecules -  $\text{SiO}_2$ , Co, metal carbonyls

Lyle D. Roelofs, Brown University, Providence, Rhode Island

Monte Carlo Simulations of Chemisorbed Overlayers

- I. Introduction
- II. Motivation for Monte Carlo Simulations of Overlayers
  - A. Results obtainable by Monte Carlo
    - 1. Phase diagrams - adatom interactions
    - 2. Critical properties
    - 3. Correlation functions - LEED results
    - 4. Effect of experimental limitations
  - B. Comparison to other methods for treating statistical systems
    - 1. Mean Field
    - 2. Renormalization Group Methods
      - a. Real Space
      - b. Migdal-Kadanoff
    - 3. Monte Carlo Renormalization Group

- III. Monte Carlo Methods for Lattice Gases
  - A. Fixed coverage
  - B. Fixed chemical potential
  - C. Pairwise and Trio interactions
  - D. Pitfalls
- IV. Monte Carlo for Systems with Continuous symmetry
  - A. Effective lattice gases
  - B. Effective molecular dynamics
- V. Monte Carlo Results
  - A. Triangular and hexagonal symmetry lattice gases
    - 1. O/Ni {111}
    - 2. H/Ni {111}
    - 3. Other systems
  - B. Square and rectangular lattices
    - 1. O/W {110}
    - 2. H/W {100}
    - 3. Other systems
- VI. Outlook and Trends

J. J. Rooney, Queens University of Belfast, Belfast, Northern Ireland

#### Relationships between Homogeneous and Heterogeneous Catalysis

Progress in understanding heterogeneous catalysis is slow because the mechanistic problems are quite formidable. We have to identify the temporary unstable intermediates involved and as well provide a structural account of the sites responsible including the atomic or ionic arrangement, the bonding of atom to atom, or ion to ion, and also to the species derived from the substrate. In other words we have to fully specify a transient unstable surface compound, its modes of formation and changes to products. Surface physics has so far been of little value in heterogeneous catalysis for obvious reasons. The transients are of necessity unstable, they are often far fewer than we believe, and finally the sites may only exist under steady-state conditions of catalyst operation. This is frequently the case with industrial catalysis and "deep" reactions in bond making and breaking. A steady-state concentration of sites are developed on the catalyst by extensive surface modification, e.g. partial reduction of oxide, carbiding of metal, sulphiding and haliding, etc. Most of the chemisorbed material in such systems does not directly participate in the catalysis but is present to sustain reactive sites, often few in number, which would not be found on the virgin surface.

Throughout my research career I have advocated the following philosophical approach in order to overcome at least in part the above problems. Catalysis at the surfaces of transition metals and their compounds is often due to the interconversion of various intermediates as

temporary unstable ligands of individual metal atoms or ions. The chemistry of these atoms and ions will be virtually the same irrespective of whether they are in a surface or solution phase. In other words each element is still uniquely the same element, and the collective electron theory as applied to ensembles and alloys is a very crude approximation. This philosophy has the immediate advantage that the relationship of heterogeneous to homogeneous catalysis and to coordination chemistry automatically follows. The second mechanistic approach which I have adopted is to choose or build model substrates which are deliberately constrained in terms of the reaction paths possible so that they can be used as probes of the projected mechanism(s). This is a popular approach to mechanism in organic chemistry.

Much of this lecture will be devoted to examples of recent work illustrating this approach and philosophy. The mechanism of the 1,2-bond-shift reaction of alkanes and cycloalkanes on transition metal catalysts will be discussed and it will be shown that the same reaction occurs in homogeneous organometallic reactions and is catalysed as well by cobalamine in vitamin B<sub>12</sub> coenzyme. New work and ideas on ethylene hydrogenation will be presented showing that the mechanism here is closer to the homogeneous mechanism than hitherto suspected. Some novel aspects of the reactions of carbonium ion intermediates on acidic surfaces will be described, highlighting the commonality of behaviour, homogeneous or heterogeneous. Finally, much recent work on metallacarbene intermediates in both homogeneous and heterogeneous systems for olefin metathesis and Fischer-Tropsch synthesis will be discussed, with emphasis on the latter as an important example where the catalytic sites are sustained by conditioning by "deep" reactions, even though carbenes are very labile and reactive intermediates.

Philip N. Ross, Lawrence Berkeley Laboratory, Materials and Molecular Research Division, Berkeley, California

#### UHV Electrochemistry

- I. Thermodynamics of Electrosorption
- II. States of hydrogen chemisorbed on Pt surfaces in solution
- III. Kinetics of hydrogen dissociation at Pt surfaces in solution
- IV. States of oxygen on Pt surfaces in solution
- V. Physical model for the structure of the Pt/H<sub>2</sub>O interface

W. E. Spicer, Stanford Electronics Laboratories, Stanford University,  
Stanford, California

Development of Photoemission as a Tool for Surface Analysis - From Semi-conductors to Catalysis

I. Question: When did photoemission become an important tool for surface studies?

II. Reference Material:

- 1903 - Einstein's landmark paper on photoemission was published
- 1921 - Einstein received the Nobel Prize (physics) for "services to theoretical physics especially the discovery of the law of the photoelectric effect."
- 1923 - Robert Millikan received the Nobel Prize (physics) for "work on elementary electric charge and the photoelectric effect."
- 1933 - Irving Langmuir received the Nobel Prize for "discoveries and investigations in surface chemistry."
- 1980 - William Spicer received the Buckley Solid State Physics Prize of the American Physical Society "for effective development and application of photoelectron spectroscopy as an indispensable tool for study of bulk and surface electronic structure of solids."

III. Question: If Nobel Prizes were awarded for photoemission and surface studies five or six decades ago, why would the APS award the Buckley Prize for its application to surfaces in 1980?

IV. General Purpose of this Paper:

To examine the historic steps and lapses which resulted in photoemission becoming "an indispensable tool" for study of surfaces.

V. Method of Approach:

To divide this century into distinct periods in which (1) the state of knowledge, (2) instrumentation (in the most general sense of the word), and (3) the "vision" of scientists, determined the range and limits set on the use of photoemission to study surfaces and absorbed species on surfaces.

To examine the way accepted theory (or the lack thereof) limited scientists' approach to problems and set the limit on their attempts to gain knowledge through photoemission.

To investigate the use of available instrumentation, the development of new instrumentation, and how this acts to limit the scientist's perspective.

To examine (through development of PES) the interaction between established knowledge, the desire for knowledge, and the tools with which it can be acquired.

# VI. The Einstein Work Function Period (ca. 1900-1935)

## A. Pure exploratory period

1. Thompson - existence of photoeffect.
2. Discovery of electron emission due to light.
3. Difficulties with vacuum, sample cleanliness, light sources, etc.
4. Attempts to determine spectral distribution of photoemission electron yield.

## B. Einstein Theory - Quantize Light

1. Maximum energy of emitted electron =  $h\nu - e\phi$  where  $e\phi$  is the potential barrier - work function.
2. Because of the theory's fundamental importance - necessity to prove or disprove experimentally.
3. Well-defined goal - drives development of experimental techniques.
4. Details of Millikan's techniques and results.

## C. Langmuir and the Development of Surface Science

1. Techniques - effect on photoemission.
2. Motivation and funding.
3. Use of photoemission.
4. General conclusions - effect on photoemission.
5. Measurement of pressure.

## D. Measuring Very Low Pressures

## E. Developments which strongly effect Theoretical Thought on Photoemission

1. Sommerfeld free electron model of a metal
2. Richard's Law of Thermionic Emission of Electrons (Nobel Prize, physics, 1928).
3. Fowler equation for spectral distribution of quantum yield near the threshold (ca. 1932 - precise determination of work function).

# VII. The Period of the Surface Photoeffect (ca. 1925-1955)

## A. Relation to Sommerfeld Theory - electron can only receive momentum from light via interaction with surface; added momentum only to surface.

## B. Detailed Quantum Theories - Mitchell, et al.

## C. Surface States

1. Tamm
2. Shockley

# VIII. Bragg Reflection, band Theory and the Volume of Photoemission (1946 - )

## A. Fan's paper (1946) - momentum conserved by Bragg reflection $\vec{k}$ conservation.

## B. Experimental Work

1. Burton -  $\text{Cs}_3\text{Sb}$ ; Apker and co-workers; Russian work - Borzak, Morguluc, and others; Mayer and alkali halides.
2. Impact of vacuum technology, Alpert vacuum gauge, measuring techniques, and optical sources.

- C. Critical Problems in Understanding Bulk Photoemission
    - 1. Mechanisms of energy loss of photoexcited electrons, phonon, electron-electron, and plasma scattering.
    - 2. Escape at surface.
  - D. Spicer's Three-Step Model
    - 1. Simplification.
    - 2. Understanding of scattering mechanisms.
    - 3. Developed to explain practical photoelectrons - important because of light sources.
- IX. Development of Photoemission as "Indispensable Tool" of Study of Bulk Electronic Structure of Solids (1962-1972)
- A. Impact of Three-Step Model
  - B. Instrumental Breakthroughs
    - 1. Vacuum technology - vac-ion dry pumps, all metal systems, reduced beaking pressure and glass problem.
    - 2. Phase sensitive detection.
    - 3. Vacuum Monochromators.
    - 4. X-ray sources and analyzer for photoemission.
  - C. Studies of Semiconductors
    - 1. Spicer and co-workers
    - 2. Allen, Gobeli, and Kane - angle resolved experiments.
    - 3. Scheer and Van Laar end surface states.
  - D. Studies of Transition Metals
  - E. Siegbahn and Development of XPS (X-ray Photoemission Spectroscopy)
  - F. Why understanding of Bulk Photoemission Spectroscopy preceded application to surfaces
    - 1. Knowledge of bulk essential before studying surfaces.
    - 2. Necessity for clean surface more demanding for surface than bulk.
    - 3. Development of radiation sources essential.
- X. Development of Photoemission Spectroscopy as an "Indispensable Tool" for Study of Surface Electronic Structure (1970-1975)
- A. The Need for High Energy Photon Sources
    - 1. Deep lying orbitals of adsorbed atoms.
    - 2. Need to separate adsorbed atoms from scattered bulk electrons.
  - B. Development of He Arc Sources for Photoemission Spectroscopy of Free Gases
  - C. Application of He Sources to Study of Adsorbed Atoms - Eastman, Nilsen, and others
  - D. Development of Synchrotron Radiation Sources
    - 1. Madden - gases.
    - 2. Wisconsin storage ring.
    - 3. Cambridge electron accelerator.
    - 4. SPEAR and the Stanford Synchrotron Radiation Laboratory (SSRL)
  - E. Application of XPS to Surface Studies
  - F. Adsorbed Versus Absorbed Gas Atoms
  - G. First Direct Observation of Full Semiconductor Filled States - Spicer, et al.; Eastman, et al. - Si
  - H. Summary of "Early" Work

# XI. Use of PES for Surface Studies Becomes Sophisticated (1975-1982)

- A. Impact of Synchrotron Radiation
  1. Continuously tunable radiation.
  2. Sampling depth of PES-Spicer, et al.
  3.  $h\nu$  dependency of matrix elements - Lindau, et al.
  4. Natural polarization.
- B. Use of Angle Resolved Photoemission and/or Polarization of Light - Smith, et al.
- C. Chemical Shifts of Molecular Orbitals of Adsorbed Atoms - Reassignments of Orbitals - Relaxation Effects
- D. Determination of Alignment of Adsorbed Molecules - Plummer, et al.
- E. Use of ARPES and Polarization of Radiation to Obtain Symmetry Information
- F. Surface States and Surface Chemistry on 3-5's - Spicer, Lindau, Hagstrum, Rowe, et al.
- G. Use of PES to Continuously Monitor Chemical Reactions - Norton, Collins, Spicer, et al.
- H. Alloys, Surface Segregation, Surfaces Adsorptions, and Catalysis
- I. Surface Extended Absorption Edge Fine Structure (SEXAFS) - Citrian-Chuck, Stohr, et al.
- J. Further Recent Developments
- K. Possible Future Developments

J. B. Uytterhoeven, Katholieke Universiteit Leuven, Leuven, Belgium

## Electronegativity: A Useful Concept in Surface Chemistry

Sanderson's electronegativity equalization principle (recently proven theoretically by Polizer and Weinstein) has shown to be especially useful for the characterization of surface properties. The effect of the composition can be quantified in a single parameter - the average electronegativity - with this restriction that for every "homologous series," a separate relationship must be established. For zeolites, the effect of the Al content, cation loading and cation type could be rationalized, irrespective of the structure type for several physicochemical properties: the acidity and carboniogenic activity of the Si-OH-Al homologous group; and the interaction of sorbed molecules with transition metal ions such as the frequency shift of the symmetric deformation band of  $\text{NH}_3$  adsorbed on  $\text{Ag}^+$  and  $\text{Cu}^+$  in zeolites for the  $\text{Ag-NH}_3$  and  $\text{Cu-NH}_3$  complexes.

J. A. Venables, University of Sussex, Brighton, Sussex, United Kingdom

The Use of Electron Microscopy in Surface Science

Techniques which use electrons as a probe or as the emitted particle, and which are surface sensitive are reviewed. By focussing the electrons such techniques can be used on a microscopic scale. The resulting methods, involving combinations of electron microscopy and surface science techniques, are widely applicable to the study of real (heterogeneous) surfaces. Recent experimental examples and possible future developments are discussed.

Emphasis is given to (i) scanning electron microscopy of surfaces; (ii) surface spectroscopies, including Auger electron and secondary electron (work-function) spectroscopy and associated microscopy; (iii) diffraction techniques (THEED, RHEED and LEED) and microscopy; (iv) photoemission and energy-loss spectroscopy, and prospects for microscopy.

Since the discussions are an essential part of ISISS, the Session Chairmen play an important role. At ISISS 1981, the following surface scientists served as Chairman:

Professor D. Lichtman  
Department of Physics and  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee

Professor R. Gomer  
The James Franck Institute  
The University of Chicago  
Chicago, Illinois

Professor R. McQuistan  
Department of Physics and  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee  
Milwaukee, Wisconsin

Professor D. Greenler  
Department of Physics and  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee

Professor G. Ehrlich  
Coordinated Science Laboratory  
University of Illinois at Urbana  
Champaign  
Urbana, Illinois

Professor D. Tong  
Department of Physics and  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee  
Milwaukee, Wisconsin

Dr. M. Kaminsky  
Surface Science Center  
Argonne National Laboratory  
Argonne, Illinois

Professor W. K. Hall  
Department of Chemistry and  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee  
Milwaukee, Wisconsin

Professor K. Watters  
Department of Chemistry and  
Laboratory for Surface Studies  
University of Wisconsin-Milwaukee  
Milwaukee, Wisconsin

One hundred and thirty scientists from all parts of the U.S.A., from Belgium, Germany, Mexico, The Netherlands, and the United Kingdom participated. They came from universities (75%), from industry (20%), as well as government institutions (5%). The educational value of the conference is demonstrated by the fact that about 45% of the participants were Graduate Students and Post-Doctoral Fellows. The registration fee was kept as low as possible.

The following registration fees were requested:

Registration before July 24, 1981:

\$55.00 Regular  
\$37.00 Graduate Students and Post-Doctoral Fellows

Registration after July 24, 1981:

\$70.00 Regular  
\$47.00 Graduate Students and Post-Doctoral Fellows

Students in the UW System paid a nominal fee.

Besides the scientific program, a number of social programs were arranged. They included dinner tours, a reception for speakers and participants from foreign countries, and a banquet. Many participants used the opportunity to visit the facilities of the Laboratory for Surface Studies at UWM. In connection with the Summer Institute, an exhibition of surface science books was organized.

International scientific societies and journals announced the conference. About 2700 scientists were contacted directly.

As in the case of former ISISS, the papers presented are published collectively in form of a single volume book. Because of the undue delay of the appearance of the ISISS 1979 Publication "Chemistry and Physics of Solid Surfaces, Volume III" (CRC-Press), another publisher was selected to publish the ISISS 1981 papers. Volume IV of "Chemistry and Physics of Solid Surfaces" is printed by Springer Verlag, Berlin-Heidelberg-New York.

ISISS 1981 was supported by grants from the University of Wisconsin-Milwaukee and a combined grant from ONR-AFOSR.

Dr. Ralf Vanselow  
Director, ISISS 1981

